Investigation of the Causes of Seasonal Variations in NO$_x$ Emissions from Waste-Coal-Fired Circulating Fluidized-Bed Utility Plants

Olayinka I. Ogunsola, Lawrence J. Shadle,* Kent Casleton, and Joseph Mei

U.S. Department of Energy, National Energy Technology Center, 3610 Collins Ferry Road, Morgantown, West Virginia 26507-0880

The results of a study aimed at identifying and understanding possible causes of seasonal variations in NO$_x$ emissions from circulating fluidized-bed (CFB) coal-fired power plants are discussed. Historical data on fuel properties, operating conditions, and emission characteristics provided by two plants were used. The extensive data were carefully and thoroughly examined and analyzed for any evidence of seasonal variations in NO$_x$ and any of the variables and relationships between NO$_x$ and the pertinent parameters. Prior to the comprehensive data analyses, a review of the literature was conducted to identify the NO$_x$ dependence parameters or variables of importance. Results obtained reveal that relatively higher ammonia was required to control NO$_x$ in the winter compared to the rest of the year at the plant that uses this compound to control NO$_x$. NO$_x$ emission and a number of operating conditions/factors (bed temperature, excess oxygen, cyclone outlet temperature, and Ca/S ratio) were observed to vary unpredictably with season, whereas a predictable seasonal variation was observed for a few other factors (humidity ratio, ammonia consumption, fuel moisture content, and ambient air temperature). Bed temperature, excess oxygen, cyclone outlet temperature, Ca/S ratio, and ammonia consumption were suspected to be related to the variations in NO$_x$ emission.

Introduction

In the mid-1980s, the development of fluidized-bed technology changed from the stationary (noncirculating) fluidized bed (SFB) to the circulating fluidized bed (CFB) mainly because of the in-bed tube erosion problems encountered in SFB boilers.[1] Other advantages of CFBs over SFBs include flexible operating conditions, the use of a wide variety of fuel, and relatively low nitrogen oxides (NO$_x$) and sulfur oxides (SO$_x$) emissions.[2] This has earned CFB technology an increasingly wide application in the waste-coal-fired power industries. The low NO$_x$ is partly due to the low combustion temperature[3] and the staged combustion capabilities, whereby the bottom part of the riser is operated fuel-rich and the top part fuel-lean.[4] The low SO$_x$ emission is achieved by the injection of a calcium-based sorbent, such as naturally occurring limestone or dolomite. However, calcium-based sorbents increase NO$_x$ emission under certain operating conditions.[1,5,6]

In general, the mechanisms for the formation of NO$_x$ and its subsequent reduction during the combustion of nitrogen-containing fuels have been thoroughly studied. Reviews of such studies involving fluidized-bed combustion systems have been published.[1,7] Although the formation of NO$_x$ during fossil fuel combustion is generally known to occur via three mechanisms (prompt NO$_x$, thermal NO$_x$, and fuel NO$_x$), NO$_x$ emission from coal-fired CFB plants is primarily due to the conversion of the fuel-bound nitrogen (FBN) to NO$_x$. It is generally recognized that FBN can be divided into two classes: (a) "volatile" nitrogen and (b) "refractory" nitrogen.[8−12] The volatile fuel nitrogen is evolved in the early stages (pyrolysis) during combustion, whereas the refractory

fuel nitrogen is burned at a later stages along with the char. The hypothetical mechanism for the conversion of FBN to NO$_x$ and N$_2$ is outlined in Figure 1.

The FBN in bituminous coal is typically divided equally between volatile nitrogen and char produced at fluidized-bed combustion (FBC) temperatures.[13,14] Volatile nitrogen is measured as HCN and NH$_3$.[1] The ratio between the two species varies with coal type.[15] During gas-phase oxidation of the volatiles at CFB temperatures, NH$_3$ is converted to NO, while HCN is mostly converted to N$_2$O. In the combustion environment, HCN and NH$_3$ are first converted to some low-molecular-weight nitrogen-containing compounds or radicals (·CN, ·OCN, ·NH$_2$, ·NH, ·N).[16−18] These intermediate species or precursors are subsequently converted to either NO$_x$ or N$_2$ through various reaction pathways, depending on the type of FBN and the operating conditions. Even though investigators disagree on the importance of individual intermediate species in FBN flame chemistry, there is consensus that they are important.[19,20]

A detailed description of the chemistry of formation and destruction of fuel NO$_x$ is given elsewhere.[21] A comprehensive study of the kinetic mechanism of reactions involving fuel NO$_x$ by Peterson and Laurendeau[17] considered 75 reactions. These mechanistic reactions for converting volatile FBN to NO$_x$ can, however, be separated into five basic steps: (1) In fuel pyrolysis and/or oxidation, the volatile nitrogen is released, while the refractory nitrogen, also known as char nitrogen, is retained with the char. (2) Volatile FBN can be converted to cyanides (R−CN), where R represents any number of substituents such as H, methyl, benzyl, etc. This reaction step is considered to be relatively fast. (3) The formation of cyanide and oxygenated cyanides (R−OCN) occurs when hydrogen cyanide (HCN), formed in step 1, is oxidized by hydroxyl or hydrogen radicals via the reactions
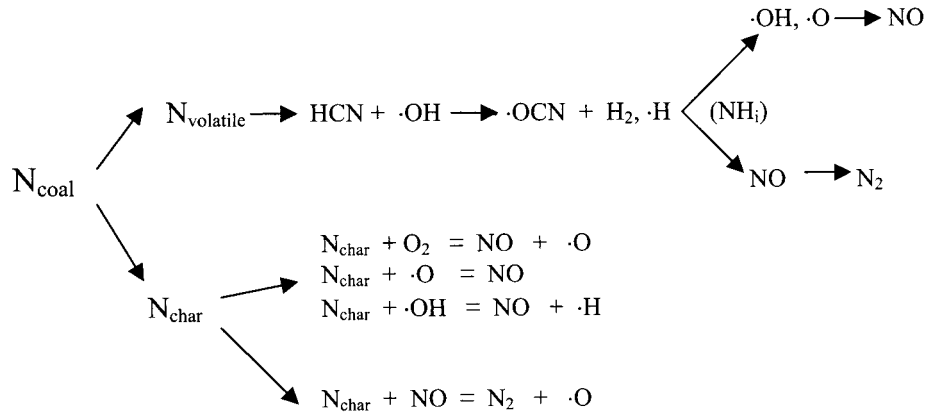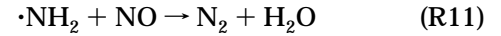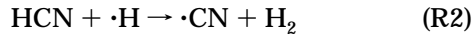
Figure 1. Potential pathways for fuel NO_x formation.

$$HCN + \cdot OH \rightarrow \cdot OCN + H_2 \qquad \text{(R1)}$$

$$HCN + \cdot H \rightarrow \cdot CN + H_2 \qquad \text{(R2)}$$
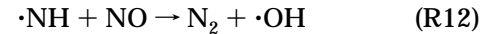
(4) Amines (NH_3, $\cdot NH_2$, $\cdot NH$) are formed from the reaction between oxygenated cyanides and hydrogen or H radical, as follows

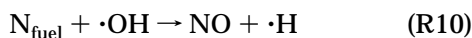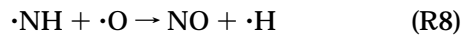$$R-OCN + H_2 \rightarrow NH_i + \text{other species}$$
$$\text{(where } i = 0-3) \quad \text{(R3)}$$

$$R-OCN + \cdot H \rightarrow NH_i + \text{other species}$$
$$\text{(where } i = 0-3) \quad \text{(R4)}$$
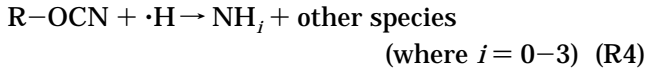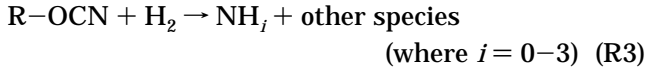
The amine species (NH_i) can react with hydrocarbon fragments to regenerate HCN

$$NH_3 + \cdot CH_2 \rightarrow HCN + 2H_2 \qquad \text{(R5)}$$

thereby continuing step 3 reactions. Also, NH_3 can be formed by the reaction of other amines with free radicals or H_2.[22] For example

$$\cdot NH_2 + \cdot OH \rightarrow NH_3 + \cdot O \qquad \text{(R6)}$$

$$\cdot NH_2 + H_2 \rightarrow NH_3 + \cdot H \qquad \text{(R7)}$$
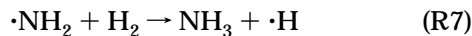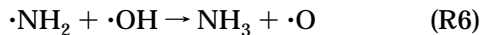
(5) Amines can be oxidized by oxidants such as O_2, $\cdot OH$, and $\cdot O$ to form NO via the reactions

$$\cdot NH + \cdot O \rightarrow NO + \cdot H \qquad \text{(R8)}$$

$$N_{fuel} + O_2 \rightarrow NO + \cdot O \qquad \text{(R9)}$$

$$N_{fuel} + \cdot OH \rightarrow NO + \cdot H \qquad \text{(R10)}$$

Combustion in a CFB boiler occurs within the riser, which functions as a staged combustion chamber.[2] As mentioned earlier, the bottom of the riser is operated under fuel-rich conditions, while fuel-lean conditions are achieved at the top of the riser.[4]

Two general NO_x reduction mechanisms in CFB boilers fired with nitrogen-containing fuel can be described: the homogeneous gas-phase and the heterogeneous solid-phase mechanisms. At the bottom of the riser (the fuel-rich zone), the conversion of volatile nitrogen species to NO_x is hindered. This is attributed to the homogeneous gas-phase reaction of evolved amines ($\cdot NH$ and $\cdot NH_2$) with NO to produce molecular nitrogen N_2 via the reactions[2]

$$\cdot NH_2 + NO \rightarrow N_2 + H_2O \qquad \text{(R11)}$$

$$\cdot NH + NO \rightarrow N_2 + \cdot OH \qquad \text{(R12)}$$

The heterogeneous NO_x reduction mechanism occurs through the reaction of the remaining unconverted NO_x, from the bottom of the riser, with N on the burning char surfaces higher up in the bed.[2] This mechanism explains the observed inverse relationship between NO_x and bed height in both pilot-scale and commercial CFB plants.[4] The mechanism for NO_x formation and reduction might be affected by operating conditions and fuel and sorbent properties.

The impact of operating conditions and some coal and sorbent properties on the conversion of FBN to NO_x during combustion in CFBs has been well studied. Reviews of some of these studies can be found elsewhere.[1,23-27] However, the effect of season on NO_x generated by coal-fired CFB boilers has not been reported in the literature. Some waste-coal-fired CFB power plants have recently observed an increase in NO_x emission during the winter season. This seasonal variation in NO_x is measured by the corresponding variation in the consumption of ammonia, which is used to reduce the NO_x emissions to within regulatory limits. The objectives of an ongoing study at the U.S. Department of Energy, National Energy Technology Laboratory (DOE/NETL), are to (a) determine the causes of the seasonal NO_x increase, (b) develop the mechanism leading to the seasonal variation, and (c) provide possible solution(s) to the problem.

Method of Approach

A series of field trips to the plants was made to better understand the problem and the operating conditions employed at the plants. After the visits, historical data on plant operating conditions and emissions characteristics were provided by the participating plants for the period of June 1997 to November 1998 by plant A and for the period of July 1993 to October 1998 by plant B. Summary reports of previous studies conducted by a third plant were also provided. Plants A and B were similar plants with different operating parameters that produced different NO_x responses to changes in the seasons. Data from these plants were compared to identify and better understand any seasonal variations.

To determine the cause(s), if any, of the seasonal NO_x variations in the CFB plants studied, it was essential to determine whether there were any seasonal variations in the plant operating conditions and/or in the
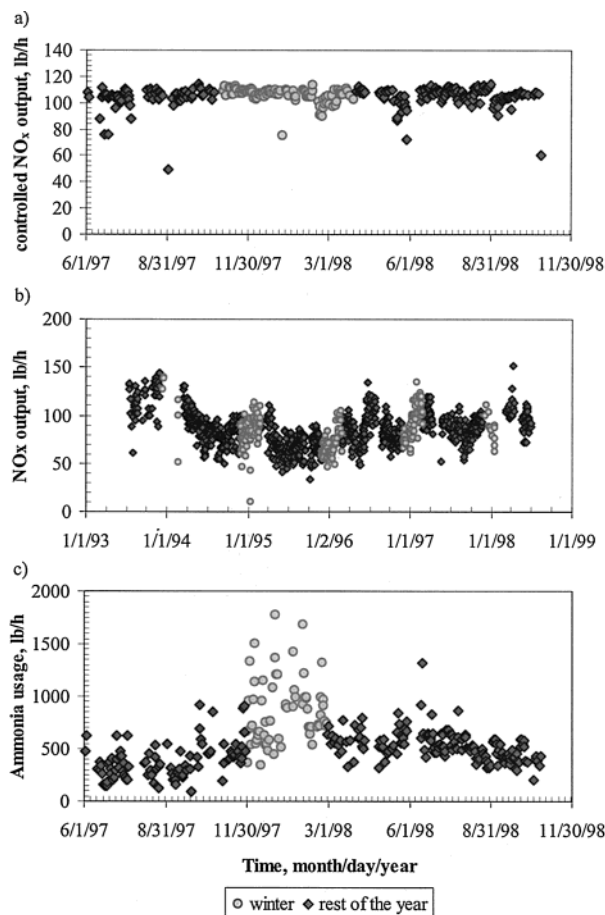
Figure 2. Variation of (a) controlled NO_x emission from plant A, (b) uncontrolled NO_x emission from plant B, and (c) total ammonia flow at plant A.

Figure 3. Variation of seasonally averaged NO_x emission from plant B.
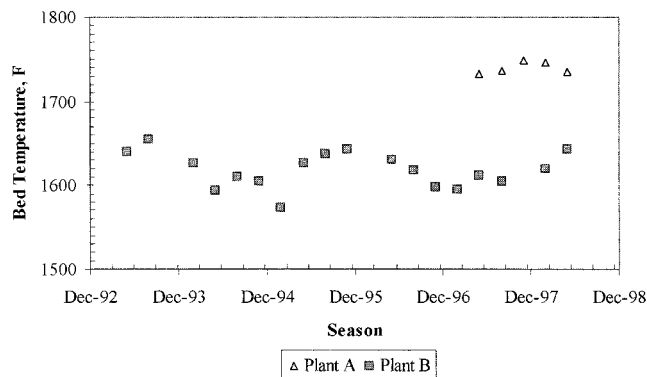
Figure 4. Variation of seasonally averaged bed temperature at plants A and B.

properties of the fuel used in the plants. As a preamble to this effort, the literature was studied to assist in choosing the most pertinent factors (operating conditions and fuel properties) that affect the conversion of FBN to NO_x in CFB boilers. The operating conditions of importance from the literature include bed temperature, sorbent (ammonia and/or limestone) injection temperature, excess air or air/fuel ratio, pressure, firing rate, sorbent feed rate, particle size of sorbent and coal, Ca/S ratio, and NH_3/NO_x molar ratio. The pertinent fuel properties that have been reported to influence NO_x emission by CFB boilers include coal type and rank; fuel nitrogen, sulfur, oxygen, and volatile matter contents; and oxygen/nitrogen ratio. The form, type, and particle size of sorbent are also known to influence fuel NO_x in CFB boilers. Although it is sometimes difficult to separate the effects of some of these factors, the results of this study and previous studies are discussed in terms of the effects of various operating parameters on NO_x emissions.

Results and Discussion

Seasonal Variation of NO_x. The controlled NO_x emitted on a daily basis by plant A is shown in Figure 2a for the period from June 1997 to November 1998, and the uncontrolled NO_x emitted by plant B on a daily basis from June 1993 to October 1998 is shown in Figure 2b. As depicted in Figure 2a, no significant daily variation in the NO_x emissions by plant A occurs. This is because the NO_x emissions at this plant were being
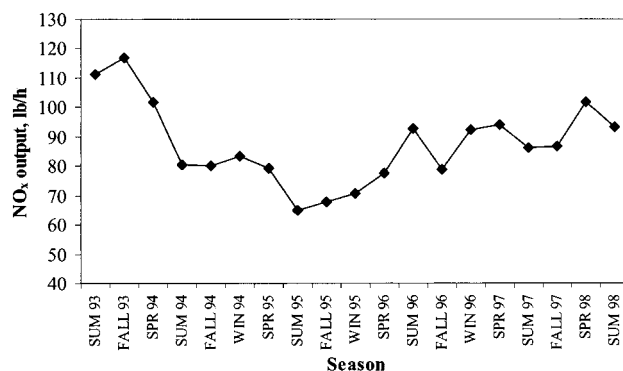
controlled to a relatively constant level by ammonia injection. Hence, ammonia usage to control NO_x at plant A was then considered to be a better variable to use for this plant, whereas the uncontrolled NO_x emission was used for plant B. The variation in ammonia usage to control NO_x by plant A from June 1997 to November 1998 is illustrated in Figure 2c.

The ammonia consumption to control NO_x emissions at plant A was highest in winter and somewhat low in summer (Figure 2c). Although the uncontrolled NO_x emission from plant B varies from time to time (Figure 2b), a predictable seasonal variation is not obvious. An analysis of seasonal averages indicated that a high NO_x band could be observed during winter 1993, spring 1995, summer 1996, spring 1997, and winter 1998 for plant B (Figure 3). Some relatively low bands of NO_x were, however, observed in summer 1994, winter 1994, summer 1995, winter 1995, summer 1997, and summer 1998.

Seasonal Variation of Factors Affecting NO_x. Having observed a higher ammonia usage for controlling NO_x in one plant and some unpredictable seasonal variations in uncontrolled NO_x emissions from another plant, we examined the available pertinent factors (operating conditions, fuel and sorbent properties) that might affect NO_x for any seasonal trend. The major factors considered were bed temperature, excess oxygen, coal type or rank, nitrogen content, sorbent injection rate, sorbent/pollutant ratio, sorbent particle size, type and form of sorbent, and sorbent injection temperature.

The variation in the seasonally averaged bed temperature is illustrated in Figure 4 for plant A and plant B. The variations in ammonia usage to control NO_x and in bed temperature for plant A are quite similar. They are both higher in the winter than in the other seasons
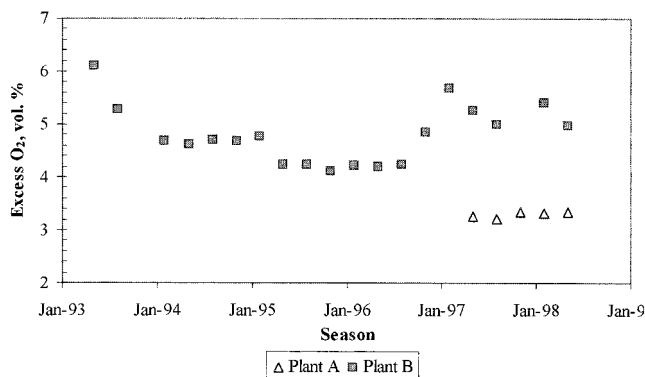
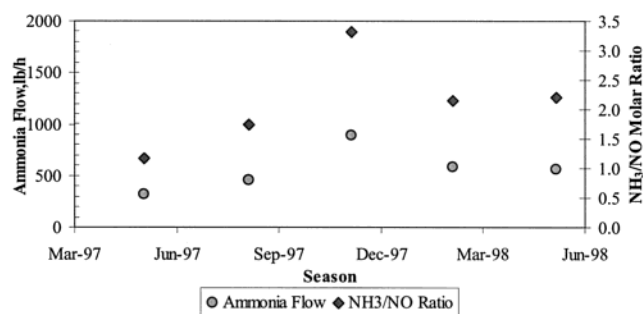**Figure 5.** Variation of seasonally averaged excess oxygen at plants A and B.

Figure 6. Variation of seasonally averaged ammonia usage and NH₃/NO ratio in plant A.

Figure 7. Variation of seasonally averaged cyclone outlet temperature at plants A and B.

Figure 8. Variation of monthly average ambient air temperature and humidity ratio for plant A.

(Figures 2c and 4). The variations in NO_x and bed temperature at plant B can be seen from Figures 3 and 4 to vary similarly for the most part of the period of study. As with the NO_x emission seasonal trend, an unpredictable seasonal variation in the bed temperature of plant B was observed. As reported in the literature,[28−31] high bed temperatures enhance NO_x production in CFB boilers.

The presence of excess oxygen promotes the oxidation of amines to NO_x via reaction R8. The variations of excess oxygen content in the flue gases with season for plant A and plant B are shown in Figure 5. Some similarity appears to exist between the seasonal NO_x trend and the seasonal excess oxygen variation for plant B from spring 1993 to fall 1998 (see Figures 3 and 5). Again, an inconsistent variation of excess oxygen with season is evident from Figure 6 for plant B. Similarly, examination of the data revealed no consistent seasonal variation in the limestone consumption or the Ca/S ratio.

Ammonia, when injected under the appropriate conditions of temperature, oxygen concentration, volatility, and NH₃/NO ratio, will reduce NO_x emissions. The variations of the daily and seasonally averaged ammonia consumption at plant A are shown in Figures 2c and 6, respectively. From Figure 2c, the amount of anhydrous ammonia consumed at plant A can be seen to be relatively higher in winter than in other seasons, as mentioned earlier. As expected, the seasonal variation in the molar NH₃/NO ratio is similar to that in the amount of ammonia injected, as can be seen from Figure 6. Other parameters at plant A that show seasonal variations similar to that of the ammonia consumption are the bed temperature and excess oxygen amount (Figures 4 and 5).

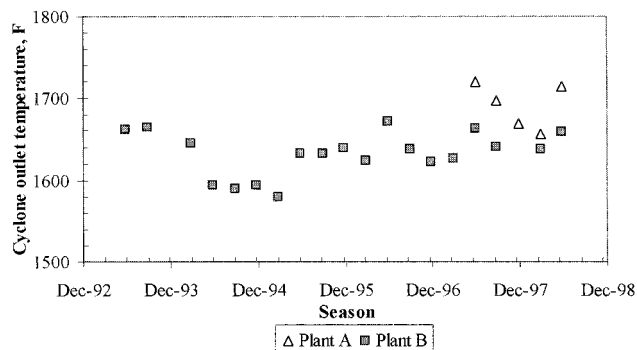Ammonia can be injected into the CFB at the inlet or outlet of the cyclone. Because the ability of ammonia to reduce NO depends on the temperature at which it is injected, among other factors, variations in cyclone temperature are expected to affect variations in the NO_x emissions. The seasonal variation in the cyclone outlet temperature is illustrated in Figure 7 for plants A and B. The cyclone temperature at plant A was relatively lower in winter and spring than in summer and fall. This trend is contrary to that exhibited by ammonia usage at this plant. This is because the effectiveness of ammonia in reducing NO_x is optimized over a narrow temperature window.[32] Injection at a low temperature (<1400 °F) reduces reduction efficiency.[32] The plant B cyclone temperature varies randomly with season and in a manner similar to the NO_x emissions from this plant (see Figures 3 and 7).
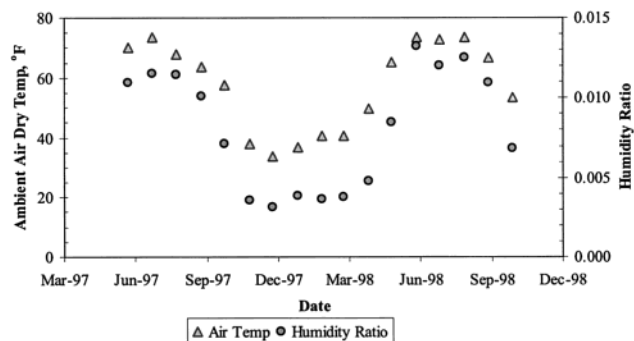
The only parameters that vary predictably with season among all of the data examined are the ambient air temperatures (wet and dry), fuel moisture, and humidity ratio. Figure 8 presents the variations of the monthly average ambient dry temperature and humidity ratio for plant A, while the seasonally averaged fuel moisture content for plant A is illustrated in Figure 9. All three parameters were found to be low in winter, when NO_x and ammonia were high. No significant seasonal variations in fuel nitrogen or sulfur were observed.

Relationship between NO_x Emissions and Pertinent Parameters. The data from the plants considered in this study and those from previous published studies were also carefully examined to determine whether any relationship exists between NO_x/ammonia usage to control NO_x and each of the parameters of importance.

(a) Bed Temperature. The effect of bed temperature on NO_x emission from a CFB boiler has been studied by a number of investigators.[28−30,33] In general, NO_x increases with increasing bed temperature regardless
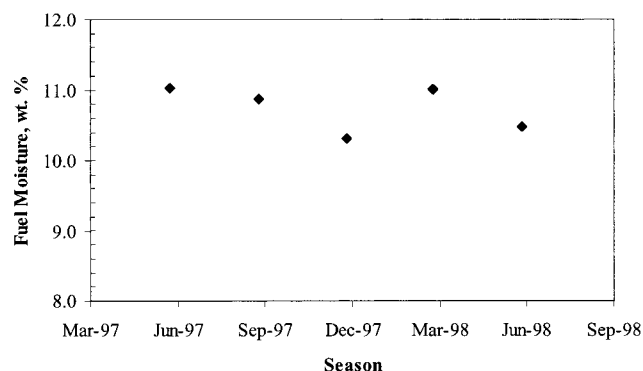
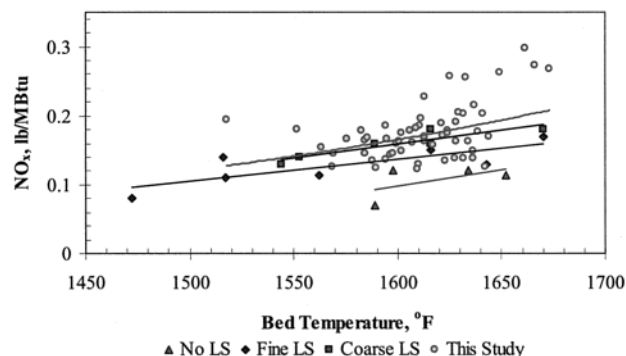**Figure 9.** Variation of seasonally averaged fuel moisture for plant A.

Figure 10. NO_x emission as a function of bed temperature from plant B in this study and from Mjörnell et al.[34] using different limestone particle size.

Figure 11. NO_x emission as a function of cyclone outlet temperature at plant B.

Figure 12. NO_x emission as a function of excess oxygen at plant B.

of coal type, air/fuel ratio,[30] and firing rate (MW),[28] as well as with or without limestone injection.[34]

The dependence of NO on bed temperature is shown in Figure 10 for plant B in this study. As expected, an increase in NO_x with increasing bed temperature is evident. This is in agreement with previous studies.[28−30,31] A similar observation was made for another commercial plant.[35] A clearer picture of the agreement between the NO_x−bed temperature relationship observed in this study and that reported in the literature is evident from Figure 10. Although the results indicate an increase in NO_x emissions with CFB bed temperature in general, the degree of linearity varies widely from study to study (from plant to plant). This general increasing trend with temperature is also most likely due to the combined effect of other factors such as coal nitrogen volatility, limestone particle size, excess air, and the presence or absence of catalytic surface (char and CaO). For example, the selectivity of HCN conversion to N_2O, in the absence of active surfaces, changes toward NO formation, and the oxidation of NH_3 to NO is enhanced in the presence of active surfaces.[1] High temperature enhances the catalytic effect of CaO in releasing volatile nitrogen as NH_3 to form NO.[28] Coarse limestone tends to produce higher levels of NO_x than fine limestone at the same bed temperature (see Figure 10).

(b) Cyclone Outlet Temperature. Typically, ammonia is injected into CFB boilers either immediately upstream or immediately downstream of the cyclone to control NO_x emissions. Limited studies on the effect of cyclone temperature (outlet or inlet) on NO_x emissions from CFB boilers exist in the literature. The relationship between cyclone outlet temperature and NO_x is shown in Figure 11 for plant B in this study. A gradual increasing trend between NO_x and cyclone outlet tem-
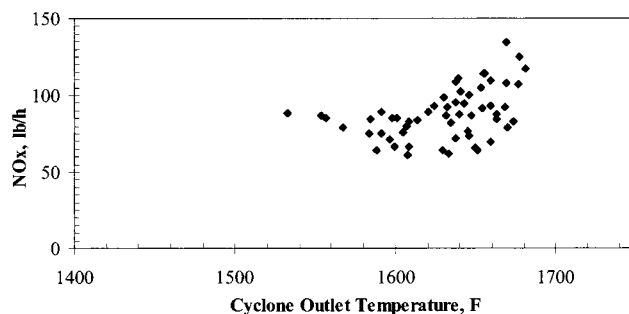
perature was observed for this plant. This is in agreement with the results reported by Gustavson and Leckner.[36] There is a narrow temperature window of about 1425−1525 °F for effective reduction of NO_x by ammonia injection.[1,32] At temperatures above the temperature window, ammonia is oxidized to NO. Below the effective temperature window, ammonia might not react with NO to produce molecular nitrogen, as expected via reactions R11 and R12.[32]
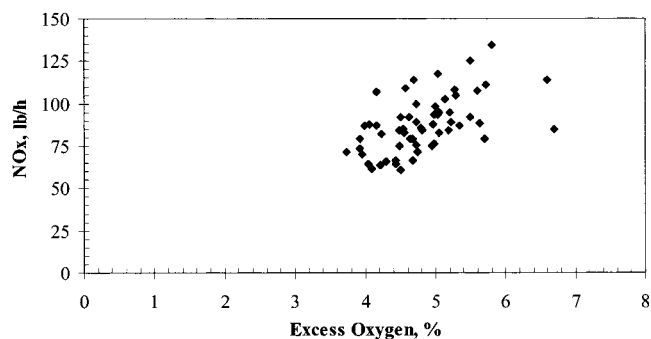
$$\cdot NH_2 + NO \rightarrow N_2 + H_2O \qquad (R11)$$

$$\cdot NH + NO \rightarrow N_2 + \cdot OH \qquad (R12)$$
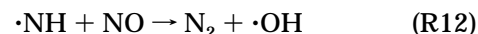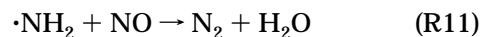
(c) Firing Rate and Load. Although no distinct relationship was observed between firing rate and NO_x emission from the plants examined in this study, NO_x emission in CFB boilers has been reported in the literature to vary with firing rate (MW) of the plant. Experimental data obtained from a 110-MW plant by Brown and Muzio[28] and from a 4-MW plant by Braun and co-workers[33] indicate that NO_x emissions in the larger plant are higher than those from the smaller plant. However, a general conclusion cannot be drawn from these studies because of the differences in the fuel and operating conditions between the two plants. The bed temperature of a large plant is usually higher than that of a small plant.[28,33] Hence, any variation in NO_x emissions from plants of different sizes is predominantly temperature-dependent. For a given plant operating between half load and full load, NO_x emissions for similar flue gas oxygen contents do not vary.[29]

(d) Excess Air. An increase in NO_x with increasing excess oxygen was observed in this study, as shown in Figure 12. Increasing the excess oxygen concentrations in a CFB has been shown in previous studies to enhance NO_x production.[28,31,37,38] The increase in NO_x emission in CFBs with increasing excess air is attributed to enhanced combustion of char in an oxygen-rich environ-

ment and lower concentrations of CO and char through-out the riser, which thus reduces the heterogeneous NO reduction reaction on the char surfaces.[31] The results obtained by Reidick and Kremer[38] indicate that the oxygen-rich combustion regime directly above the bottom nozzle plate is the most important region for NO formation. Any operating conditions that inhibit good mixing in this region enhance the oxygen-enrichment, thus leading to NO_x in that region.

In addition, free radicals ($\cdot OH$, $\cdot H$, and $\cdot O$) play important roles in the chemistry of fuel nitrogen conversion, as demonstrated by reactions R4, R6, R8, and R10, as well as those shown in Figure 1.[22] Whether fuel nitrogen is converted to NO instead of N_2 during homogeneous reactions depends on the concentrations of $\cdot OH$ and $\cdot O$ radicals.[38] Higher concentrations of these radicals favor NO formation, whereas lower concentrations favor N_2 formation.[38] Whereas the absence of these chain-propagating radicals inhibits NO formation, the presence of any scavenger of these free radicals will jeopardize the effectiveness of staged combustion in controlling NO_x.[22] For a staged combustion system to be effective in reducing NO_x emissions, it is important to convert the fuel nitrogen as early as possible in the first stage (typically the bottom of the riser) to NO_x, which will subsequently be converted to N_2 via eqs R11 and R12. The presence of excess oxygen will enhance the oxidation of NH_i species to NO_x via reaction R8. Also, oxygen-rich conditions lead to reduced concentrations of char and CO, which could promote[31] the formation of N_2O and N_2.

(e) Limestone Injection. The removal of SO_2 by limestone generally occurs via two successive reaction steps, namely, calcination and sulfation of the limestone particles[39]

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (R13)$$

$$CaO(s) + SO_2(g) + 0.5O_2(g) \rightarrow CaSO_4(s) \quad (R14)$$
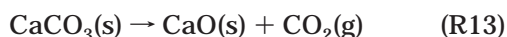
However, the addition of calcium-based sorbent has been shown to catalytically enhance NO_x emissions in CFB boilers.[1,5,39,40] If CaO is present in excess of what is required for the sulfanation reaction (eq R14), the unreacted CaO becomes a principal catalyst for oxidizing FBN to NO_x.[3,23,39,41]

The factors that influence SO_2 capture efficiency, which in turn impact NO_x emission, include the type, form, and particle size of the injected Ca-based sorbent; the injection temperature, the fuel type, and the sorbent injection location. These factors can vary from time to time and even seasonally at a plant that obtains its limestone from external sources. The effect of Ca/S ratio on ammonia usage to control NO_x and/or NO_x emissions from plants A and B in this study is illustrated in Figure 13. For both plants, ammonia usage/NO_x increased somewhat with increasing Ca/S ratio. In general, SO_2 capture efficiency by limestone injection decreases with increasing temperature above a certain temperature for maximum efficiency.[31,42] The temperature at which maximum efficiency is achieved varies depending on the type and particle size of the sorbent, the coal type, and the boiler operating conditions. Sulfur dioxide capture efficiency peaks between 900 and 950 °C and between Ca/S ratios of 3 and 4. Capture efficiency decreases and NO_x emission increases with increasing feed rate and particle size of Ca-based sorbent and with increasing Ca/S ratio beyond about 3.[31,42] Similarly, coals with high
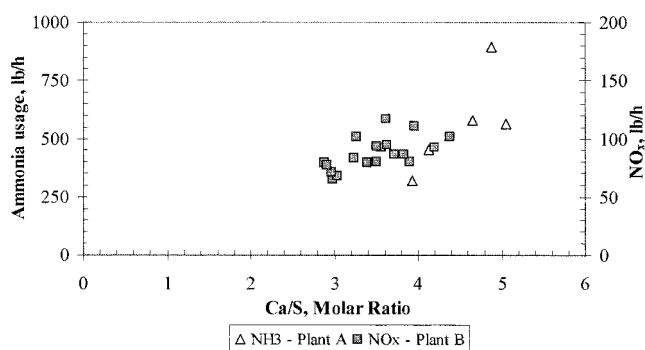

Figure 13. Seasonally averaged ammonia usage (plant A) and NO_x emission (plant B) as a function of Ca/S molar ratio.
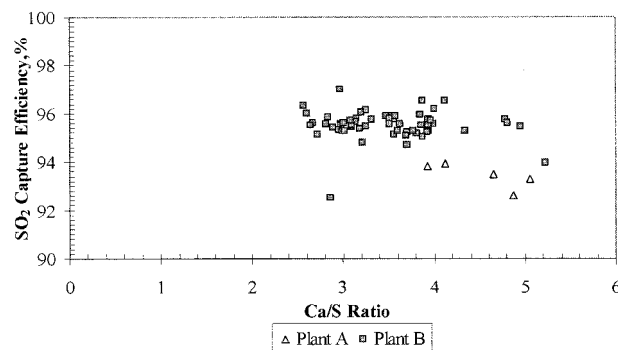

Figure 14. Sulfur dioxide capture efficiency as a function of Ca/S molar ratio at plants A and B.

inherent Ca contents and low sulfur contents will require smaller Ca/S ratios and limestone feed rates than coals with low calcium and high sulfur contents before running the risk of increased NO_x. This is in agreement with the results observed by Brown and Muzio.[28] Normally, HCN favors N_2O formation, whereas NH_i species are important sources of NO_x during the combustion of nitrogen-containing fuel.[1] In the presence of unreacted CaO, however, the route of HCN-to-N_2O changes toward the HCN-to-NO_x route,[5,43] and the oxidation of NH_i to NO is enhanced.[41,44] The conversion of HCN to NH_3 by hydrolysis over surfaces such as CaO or char has also been reported.[45] The NH_3 is then oxidized to NO elsewhere in the combustor in the presence of oxygen.[1] The results of a series of tests in a CFB reveals a higher capture efficiency (that is, lower NO_x emission potential) with finer coal particles.[46] It was observed for a 40-MW CFB boiler that crystalline limestone was found to increase NO_x less than porous limestone.[34] Although the addition of limestone increases NO_x emissions in a CFB boiler, the rate of increase decreases along the height of the riser.[31]

The effect of the Ca/S ratio on the SO_2 capture efficiency for plants A and B is shown in Figure 14. A decrease in the capture efficiency could be observed for plant A as the Ca/S ratio increased from about 3.5 to about 5.5. No significant change in the capture efficiency at plant B was observed with increasing Ca/S ratio above 2.5, as illustrated in Figure 14. These observations imply that the Ca/S ratio at plant B had reached its optimum value, whereas plant A has exceeded its optimum Ca/S value. The reason for the lower capture efficiency at plant A than at plant B is partly due to the higher bed temperature at plant A.

The effect of temperature on the relationship between the Ca/S ratio and the amount of ammonia needed to control NO_x, shown in Figure 15, suggests higher
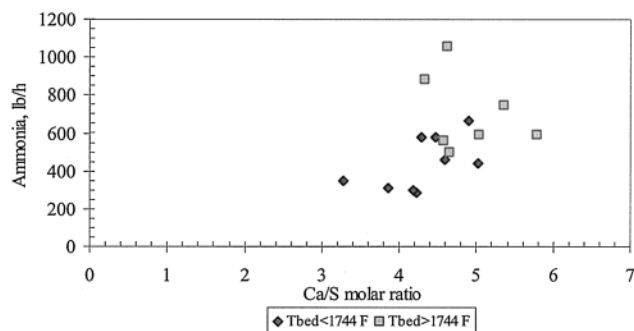
Figure 15. Monthly averaged ammonia usage as a function of Ca/S molar ratio at plant A.

Figure 16. Monthly averaged NO_x emission as a function of ammonia usage at plant A.

ammonia usage at high temperatures than at low temperatures for the same Ca/S ratio. The effectiveness of the two sorbents (ammonia and limestone) in reducing the respective pollutants (NO_x and SO_2) is reduced at high temperature, thereby leading to excessive concentrations of these species and, subsequently, to increased NO_x. These properties can vary with season because the limestone is obtained through various external sources. However, data are not available to establish any consistent seasonal variation in the type and particle size range of the limestone supplied to the plants of this study.

(f) Ammonia Injection. Ammonia is injected into CFB boilers to reduce NO_x emissions through reactions R15 and R16

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (R15)$$

$$4NH_3 + O_2 + 4NO \rightarrow 5N_2 + 6H_2O \qquad (R16)$$
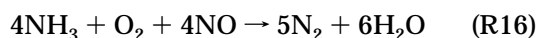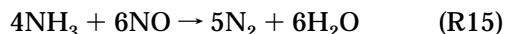
Its effectiveness, however, depends on the temperature at which it is injected, the form in which it is injected, and the quantity injected. To be optimally effective, it must be injected within a narrow temperature range that varies with the form and type of ammonia, the NH_3/NO ratio, and the coal type. Ammonia can be injected in aqueous or powder form. In aqueous form, it must be in the appropriate concentration, and it must be volatilized properly prior to or during injection. The volatility and effectiveness of ammonia can be relatively low in winter. Low concentrations and improved volatility have been observed to reduce ammonia consumption by some CFB boilers.[35] As in the case of limestone, if the capture efficiency is low, there will be more ammonia than required in the system, and the excess can be oxidized to NO_x elsewhere in the system via the reaction

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (R17)$$
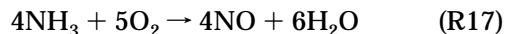
The relationship between NO_x and ammonia consumption at plant A in this study is illustrated in Figure 16. An increasing band of NO_x with ammonia could be seen under low-temperature conditions, whereas the trend at high temperature is not well defined. Also, relatively more ammonia is required at high temperatures than at low temperatures to control the same level of NO_x (Figure 16). This suggests that the mechanism for NO_x reduction at low temperature might be different from that at high temperature.

The results of a previous study aimed at investigating the effect of ammonia injection on reductions of NO_x emissions in a coal-fired stationary FB boiler show that
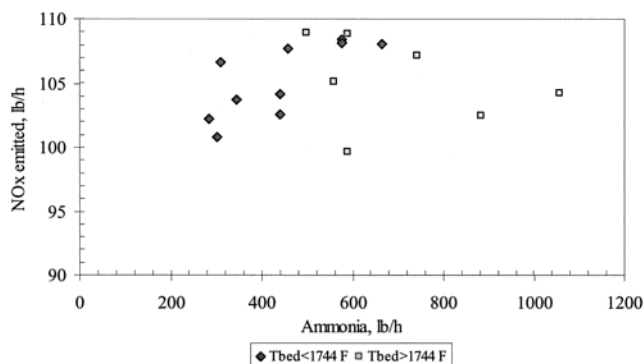
a greater NO_x reduction can be achieved with aqueous urea than with aqueous ammonia.[33] NO_x reduction increased exponentially with increasing NH_3/NO molar ratio for both aqueous ammonia and aqueous urea.[33] However, the NH_3/NO ratios at which no further significant reduction occurred differed, being about 0.8 and 3, respectively, for urea and ammonia.[33] The results obtained in a pressurized fluidized-bed boiler by Jahkola et al.[32] indicate a decrease in NO_x with increasing NH_3/NO molar ratio up to a certain point, beyond which no further decrease in NO_x with further increase in NH_3/NO molar ratio is evident. The optimum NH_3/NO molar ratio for maximum reduction in NO_x was reported to vary with fuel type, being 4:1 for peat and 3:1 for coal.[32] The effectiveness of ammonia injection in reducing NO_x is also influenced by the conditions (temperature and oxygen concentration) at the point of injection, as discussed earlier. Furthermore, injection at a point where the temperature and oxygen concentrations are high enhances oxidation of the injected ammonia to NO_x rather than reducing NO_x. This is probably why higher amounts of ammonia were needed at high temperature to control NO_x at plant A (Figure 16). Ammonia injection at a low-temperature point (<1400 °F) will lower the reduction efficiency.[32]

(g) Coal Properties. Coal properties that have been identified as impacting the conversion of FBN during combustion include coal rank; volatile matter, nitrogen, sulfur, and mineral matter contents; oxygen/nitrogen ratio; and coal nitrogen content. As expected, a review of the literature reveals an increase in NO_x emission from burning nitrogen-containing fuel with increasing nitrogen contents. This is in agreement with the FBN–NO_x emission relationship observed for plant A in this study (see Figure 17). However, as illustrated by the results of this study shown in Figure 18 and supported by the results of others,[22,47,48] the fraction of FBN converted to NO_x decreases with increasing FBN. As explained by others,[22,47,48] this is probably because the percentage of volatile FBN in the total amount of FBN decreases as the FBN content decreases.

The relationship between NO_x emission and fuel moisture at plant B in this study is illustrated in Figure 19. Despite the presence of considerable scatter in the data, a decrease in NO_x with increasing fuel moisture is suggested. This implies that a low moisture in the coal and combustion air, as shown by the seasonal variation in fuel moisture and humidity ratio (Figure 8), might yield a low concentration of superequilibrium free radicals (·O, ·H, ·OH). Low concentrations of superequilibrium free radicals have been shown to impact FBN-to-NO_x chemistry.[49]
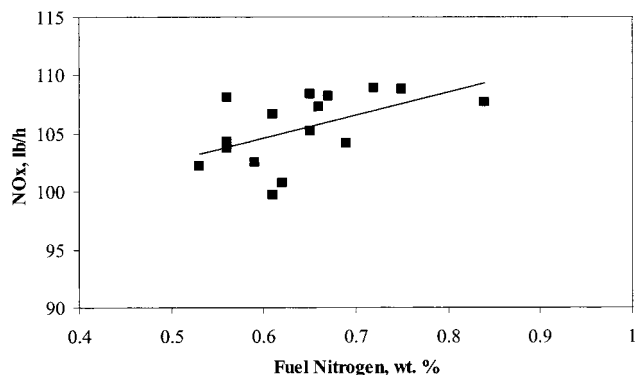
Figure 17. Monthly averaged NO_x emission as a function of fuel nitrogen at plant A.
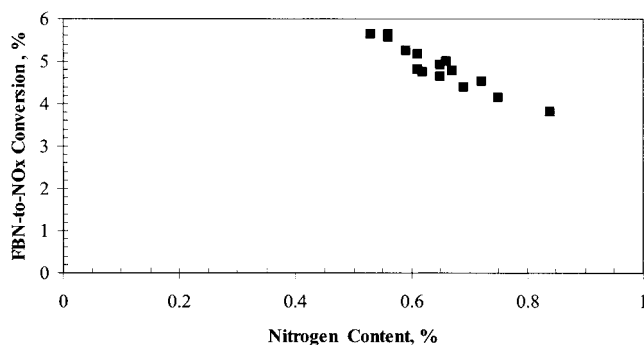

Figure 18. Fuel nitrogen-to-NO_x conversion efficiency as a function of fuel nitrogen for plant A.
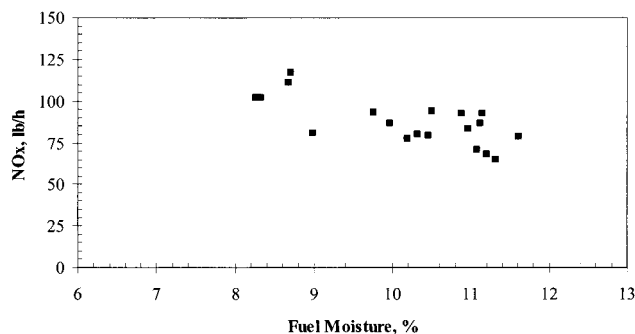

Figure 19. Seasonally averaged NO_x emission as a function of fuel moisture at plant B.

The impact on NO_x of other coal properties that have been reported in previous studies is also discussed here. The direct impact of fuel sulfur content on NO_x formation during combustion has been a controversial issue.[22,48,50] However, sulfur dioxide has been shown to be an effective catalyst in reducing the superequilibrium concentrations of ·H, ·O, and ·OH free radicals.[49] These free radicals play important roles in the chemistry of nitrogen conversion during the combustion of nitrogen-containing fuels, as can be seen from the reaction mechanisms listed in this paper and shown in Figure 1. Their presence has been shown[51] to enhance the rate of conversion of total fixed nitrogen (TFN) (TFN = $HCN + NH_3 + NO_x$) into N_2. Therefore, it is expected that SO_2, and possibly other sulfur compounds, will inhibit NO_x formation and that NO_x will decrease with increasing fuel sulfur content. However, the results of previous studies[43,49] have shown that fuel sulfur can inhibit or enhance NO_x formation. Another way fuel sulfur can influence NO_x emissions is through operation above the optimum Ca/S ratio and/or limestone feed rate required for maximum SO_2 capture efficiency. This will

lead to the presence of excess unreacted CaO and increased NO_x emissions. It is particularly easy to run into this situation when the fuel sulfur content is low and/or the fuel is rich in calcium.

Low-rank coals (LRCs) are relatively more reactive and have higher volatile matter, oxygen, and inherent calcium contents and lower sulfur contents than high-rank coals (HRCs). High reactivity will result in lower concentrations of char, which is a catalyst for the heterogeneous decomposition of NO_x and N_2O.[29] The char of LRCs has also been observed to have a greater catalytic tendency to reduce N_2O because of its fine dispersed mineral matter.[52] Also, LRCs tend to release most of their FBN as NH_3, which is easily oxidized to NO_x, whereas most of the HRC's FBN is released as HCN.[29] Volatile FBN is rapidly converted to NO, whereas char FBN is slowly converted to N_2O.[25] Therefore, high-volatile-matter coal is expected to favor production of NO rather than N_2O. This agrees with the results observed by Kramlich and Linak.[25] Although high-volatile coals generally produce more NO than low-volatile coals, no correlation exists between NO_x and coal volatile matter content.[30] However, NO_x was found to correlate well with fuel ratio, that is, fixed carbon/volatile matter ratio.[30] Another impact of a high-volatile coal is its devolatilization at a different location than low volatile coal in the riser of a CFB as a result of its (low volatile coal's) high volatile matter and low thermal decomposition temperature.[29] Release of the volatile-containing predominantly amine species in the oxygen-rich zone of the riser will lead to increased NO_x emissions in that region. In a CFB, an oxygen-rich zone can occur as a result of improper mixing. Improper mixing can occur from malfunctioned air- and/or fuel-injection/distribution systems. Mixing has been observed to occur at locations as high as 10 m above the gas distribution plate in the riser of a CFB.[1,31] Any cause of a change in this location, which might occur from time to time, can impact FBN-to-NO_x chemistry. Coals with high inherent calcium contents and low sulfur contents, such as low-rank coals, need relatively less additional limestone to meet the SO_2 limits. Hence, it is easy to have excess CaO, thereby increasing NO_x emissions.

Fine coal particles burn faster and more readily than coarse coal particles. It is therefore expected that less char, the presence of which changes the FBN conversion route from $FBN-HCN-N_2O$ to $FBN-NH_3-NO_x$, will be present with fine particles, thereby resulting in lower NO_x emissions. This is in agreement with the results reported by de Diego and co-workers,[31] who observed an increase in NO_x emissions with increasing coal particle size. Hence, any plant operation that affects the feed coal and sorbent particle size might contribute to the NO_x variation.

Conclusions

Data on NO_x emission characteristics and plant operating conditions of waste-coal-fired CFB power plants have been examined and analyzed to investigate the possible causes of seasonal variations in ammonia usage to control NO_x at these plants. In addition, a review of factors affecting NO_x emissions from coal-fired boilers is provided. For plant A, ammonia consumption to control NO_x was highest in the winter season than in other seasons. A number of the pertinent operating conditions/parameters varied with season. However, the variations of many of these factors were unpredictable,

whereas the variations of a few others were predictable for the plants studied. The parameters with predictable seasonal variations were ammonia consumption, ambient air temperature, fuel moisture content, and humidity ratio. Those with unpredictable seasonal variations were bed temperature, excess oxygen amount, Ca/S ratio, limestone injection rate, ammonia/NO ratio, fuel nitrogen and sulfur contents, and NO_x emission. For plant B, predictable relationships were evident between NO_x and bed temperature, excess air, cyclone outlet temperature, and Ca/S ratio. For plant A, predictable relationships were evident between ammonia consumed and bed temperature, excess air, cyclone outlet temperature, and Ca/S ratio. In comparing the NO_x emission from plant B to the ammonia usage in plant A, it was observed that plant A operated at higher temperatures and Ca/S ratios and exhibited seasonal variations in ammonia usage, whereas plant B exhibited little or no seasonal trend for NO_x release.

The possible cause of the seasonal variation in NO_x and/or ammonia needed to control NO_x emission is a combined effect of variation in bed temperature, sorbent injection temperature, excess oxygen, Ca/S ratio, and fuel. Other probable causes supported by data from previous studies are sorbent and coal particle size; sorbent volatility, type, and form; and ammonia consumption. It is proposed that the moisture balance (i.e., air moisture plus fuel moisture) can affect the super-equilibrium concentration of the free radicals, which impacts FBN-to-NO_x chemistry. Winter consumption of ammonia to control NO_x emissions has been reduced at another waste-coal CFB power plant by improving the volatility of the aqueous ammonia injected.[35] In addition, NO_x emissions were reduced by decreasing the bed and cyclone temperatures by improving the cyclone efficiency and air distribution at another commercial CFB plant and by steam injection at a third plant. The Ca/S ratio was also reduced by these modifications. It is, therefore, of practical benefit to operate CFBs at lower but optimum conditions (bed temperature, sorbent injection temperature, excess oxygen, Ca/S ratio) and, if this is not possible, to increase the fuel and air moisture contents to reduce emissions.

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